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Faradaic Rectification Studies on Tl^{+}-Tl^{3+} Redox Couple at the Platinum Electrode Interface

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The kinetic parameters involved in the Tl^{+}, Tl^{3+} redox couple at the Pt electrode in different supporting electrolytes, viz. $HClO_4$, H_2SO_4, HCl and KNO_3 have been obtained using the faradaic rectification method. These parameters have been obtained by the zero-point method also and the results support those obtained by the extrapolation method. The values of transfer coefficients obtained by the extrapolation method are slightly lower but those of the rate constants are about 1·5 to 3 times lower as compared to the values obtained by the zero-point method. The values of rate constant obtained by zero-point method for ClO_4^-, SO_4^{2-}, Cl^- and NO_3^- anions are 0·33, 0·27, 0·16 and 0·10 cm/sec respectively. The value of α for ClO_4^- and SO_4^{2-} is 0·56 while it is 0·53 for Cl^- and NO_3^-. The mechanism of the reaction is quite complex because Tl(I) is strongly adsorbed at the platinum interface and, therefore, the kinetic parameters reported are for the overall reaction.

THE asymmetry in the current-potential curve can arise either due to inequalities in the mass transfer rates of the oxidants or reductants, or due to the asymmetry of the charge-transfer reaction resulting in the rectification effects now commonly known as faradaic rectification[1,2].

The earlier studies on faradaic rectification have mostly been carried out on systems involving one-electron charge-transfer processes and only a few studies have been carried out on systems involving two-electron charge-transfer processes, using d.m.e.[3] or hanging amalgam drop electrode[4]. The mechanism of the multiple electron charge-transfer involved in the reaction was not considered in the studies. Due to the apprehension of adsorption of impurities and specific adsorption of the reactants at the metal (solid) electrodes, such studies have generally been neglected with the consequence that the theoretical knowledge of the role of inert metals in the mechanism of the process, is not well understood. A number of workers[5-7] have studied the Tl^{+}, Tl^{3+} redox couple at the platinum surface using different methods and determined the kinetic parameters corresponding to two steps each involving one-electron charge-transfer. The values of rate constants obtained corresponding to two steps are not very different, and this adds to the complications in interpreting the results on the basis that one of the two reactions is slower and overall rate-controlling.

Recent observations of James[8] specifically mention that Tl(I) is excessively adsorbed at the platinum surface and it would affect the correct determination of kinetic parameters. In continuation of our studies on several single electron charge-transfer redox couples[9,10] at the metal electrode interface using the faradaic rectification method, the work is extended to Tl^{+}, Tl^{3+} redox couple in different supporting electrolytes at platinum electrode interface.

The ionic strength of the supporting electrolyte was kept much higher (1·0*M*) compared to that of the electroactive species (1-3 m*M*) so that post-separation of the double layer would not be much involved[3].

Determination of kinetic parameters, independent of the values of double-layer capacitance, electrical impedance and electrode solution interfacial potential, is possible if zero-point method[11,12] could be used. Wherever possible this method has been used for determining kinetic parameters for the Tl^{3+}, Tl^{+} redox couple in different supporting electrolytes.

Materials and Methods

All the solutions were prepared from AR reagents in triply distilled water. Thallic salt solutions were prepared by the oxidation of thallous salt solutions of known strengths. Solutions of supporting electrolytes were treated with purified activated charcoal[3] and only the clear decanted solutions were used. Purified nitrogen was bubbled through the solutions for 30 min prior to each experiment. The supporting electrolytes were 1·0*M* $HClO_4$, 0·5*M* H_2SO_4, 1·0*M* HCl and 1·0*M* KNO_3.

The cell and experimental techniques used for the study were the same as described earlier[13]. The three platinum electrodes used were pretreated and tested for their suitability for such studies in the same way as described earlier[13]. McBain-Dowson cell was used to determine the diffusion coefficient (D). The value of D is found to be $9{\cdot}6 \times 10^{-6}$ cm^2/sec in 1·0*M* $HClO_4$.

Results and Discussion

The nature of the curves obtained by plotting $\Delta E \propto / V_A^2$ against $\omega^{-\frac{1}{2}}$ in different supporting electrolytes, is similar (Fig. 1). All the curves tend to be linear in the frequency range above 5 KHz. These linear

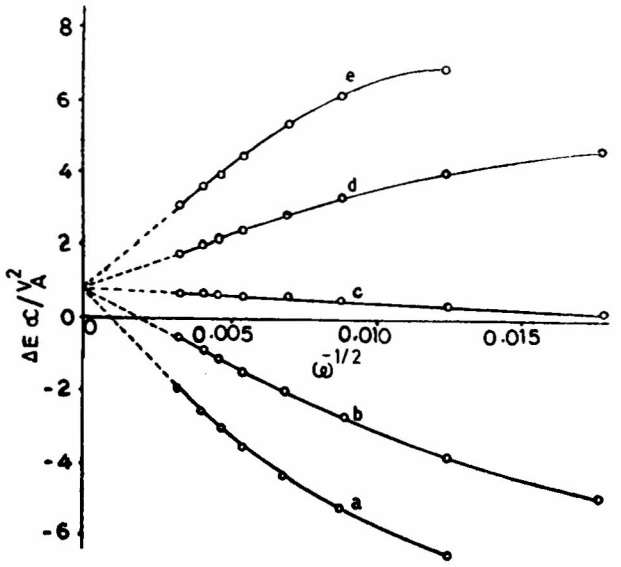

Fig. 1 — Plots between $\Delta E_\alpha / V_A^2$ and $\omega^{-1/2}$ for Tl^+, Tl^{3+} couple in 1·0*M* $HClO_4$/Pt [Tl^+ (m*M*)/Tl^{3+} (m*M*) = (a) 2/0·5; (b) 2/1; (c) 1/1; (d) 1/2; (e) 0·5/2]

plots, on extrapolation, converge to the same point on the ordinate. From the magnitude of the intercept, the value of α can be determined using Delahay's expression[14] (1), assuming that both the electrons are involved in a single rate-determining step

$$\frac{\Delta E_\omega}{V_A^2} = \frac{nF}{RT}\left[\frac{2\alpha-1}{4} - 1/2\left\{\frac{C_O^\circ D_O^{1/2}}{C_O^\circ D_O^{\frac{1}{2}} + C_R^\circ D_R^{\frac{1}{2}}}\right\}\frac{1}{p}\right]$$

where

$$p = \frac{2^{1/2}\omega^{1/2}}{k_a^\circ} \frac{C_O^{\circ\alpha} \times C_R^{\circ(1-\alpha)} \times D_O^{1/2} \times D_R^{1/2}}{C_O^\circ D_O^{1/2} + C_R^\circ D_R^{1/2}}$$

In the above equation ΔE_ω is the rectified potential; V_A is the a.c. potential at the electrode-solution interface; α is transfer coefficient; $\omega = 2\pi f$, f being the frequency of a.c.; C_O°, C_R°, are the concentrations and D_O and D_R are the diffusion coefficients of the oxidant and reductant respectively; k_a° is the rate constant, n is the number of electrons involved in the charge-transfer reaction and F, R and T have their usual significance.

It is evident from the values of rate constant, obtained by the earlier workers[5,6], for the two steps (2) and (3) that these are not very different.

$$Tl^{3+} + e = Tl^{2+} \quad ...(2)$$

$$Tl^{2+} + e = Tl^{+} \quad ...(3)$$

Thus, kinetic parameters obtained in the present study are for the overall reaction.

From the intercepts of the curves on the abscissa (Fig. 1), the zero-point frequencies (at which the rectification becomes zero) were determined and have been used in calculating the values of kinetic parameters by the zero-point method[12]. The values obtained are given in Table 1.

The values of kinetic parameters were similarly evaluated from the solopes of corresponding plots of $\Delta E\alpha / V_A^2$ against $\omega^{-\frac{1}{2}}$ in H_2SO_4, HCl and KNO_3 media and they are given in Table 1. It is interesting to note that the values of α are not influenced by the nature of anions. However, the values of k_a° in the different supporting electrolytes decrease in the order: $HClO_4 > H_2SO_4 > HCl > KNO_3$.

Table 1 — Kinetic Parameters of Tl^{3+}, Tl^+ Reaction at the Platinum Interface

[Values reported for 6·5*M* H_2SO_4 are at 25° and the rest of the values are at 27°]

Supporting electrolyte	Conc. of redox couple (m*M*) Tl^{3+}: Tl^+	$\alpha^\dagger$ (cathodic) (expt)	k_a° cm/sec (expt)	$k_a^{\circ\ddagger}$ (cm/sec)
$HClO_4$ (1·0*M*)	0·5: 2·0	0·52	0·12	0·33
	1·0: 2·0	(0·56)	0·12	
	1·0: 1·0		0·20	
	2·0: 1·0		0·10	
	2·0: 0·5		0·12	
H_2SO_4 (0·5*M*)	0·5: 2·0	0·52	0·11	0·27
	1·0: 2·0	(0·56)	0·11	
	1·0: 1·0		0·11	
	2·0: 1·0		0·10	
	2·0: 0·5		0·11	
H_2SO_4 (6·5*M*)		0·36*		
HCl (1·0*M*)	0·5: 2·0	0·52	0·10	0·16
	1·0: 2·0	(0·53)	0·10	
	1·0: 1·0		0·09	
	2·0: 1·0		0·09	
	2·0: 0·5		0·10	
KNO_3 (1·0*M*)	0·5: 2·0	0·52	0·08	0·10
	1·0: 2·0	(0·53)	0·08	
	1·0: 1·0		0·08	
	2·0: 1·0		0·07	
	2·0: 0·5		0·08	

*Tafel plots, ref. 5.
†Values in parentheses are from zero-point method.
‡Values from zero-point method.

The values of rate constants obtained by zero-point method are also found to vary in the above order in different media. However, the values are 1·5 to 3 times higher than those obtained by extrapolation method. It is to be noted that the values of α as determined by the zero-point method in $HClO_4$ and H_2SO_4 media are somewhat higher than those obtained in HCl and KNO_3. The values of α obtained by zero-point method are in general somewhat higher as compared to those obtained by the extrapolation method.

It is rather surprising that the values of rate constants determined by faradaic rectification method are of the order of 10^{-1} cm/sec as compared to those reported earlier[5] which were of the order of 10^{-4} cm/sec. This divergence is probably due to the excessive adsorption of Tl^+ ions at the metal electrode interface and differences in the pretreatment of the electrode[8].

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